

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN SHOE MANUFACTURE

(71) We, THE SHOE AND ALLIED TRADES RESEARCH ASSOCIATION, a British company, of Satra House, Rockingham Road, Kettering, Northants, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to the adhesion of elastomeric materials, and in particular to the attachment of shoe sole material to shoe upper material such as leather.

15 It is known that the receptiveness of elastomeric soiling material (e.g. natural rubber, styrene-butadiene rubber, nitrile rubber, and mixtures and blends of these), towards adhesives of, e.g. polychloroprene and polyurethane types, is often unsatisfactory. Modern methods of shoemaking frequently employ stuck-on soles, as opposed to the traditional stitched-on leather sole and hence the problem of ensuring good adhesion of the sole to the upper is of considerable importance.

20 British Patent Specification Nos. 1,278,258, 1,295,677, and 1,295,842 describe various ways of improving adhesion by halogenating the rubber surface e.g. through the use of an organic halogen donor which liberates halogen slowly.

25 The treatment described generally consists of wiping or dipping the elastomeric sole material in a solution containing the halogen donor, after which the sole is dried and can be stored prior to attachment to the shoe upper. A sole may be pre cemented after such treatment and subsequently heat activated before securement.

30 It has been proposed in British Patent Application No. 54751/72 (Serial No. 1458007) to incorporate in a polyurethane adhesive both a small proportion of an organic bromine donor and an organic isocyanate or "primer". The adhesive so formulated gives rise to acceptable creep

resistance at elevated temperatures. The invention of the latter application is of particular value for bonding thermoplastic rubbers of the block-copolymer type as no pretreatment of the bonding surface is necessary before application of the adhesive.

35 The inventions of the above-mentioned patent specifications are entirely concerned with the adhesion, e.g. to shoe uppers of ready-made moulded soles.

40 An alternative practice has now arisen of directly injection moulding thermoplastic elastomer soles to shoe uppers in a similar manner to the relatively older practice of the injection moulding *in situ* of PVC soles. By "thermoplastic elastomer" is meant generally any injection mouldable rubber-like material.

45 The present invention, as will become apparent, is concerned with thermoplastic elastomers containing EVA (ethylene-vinyl acetate copolymer) whether in pure form or admixed with other thermoplastic elastomers and/or compounding materials.

50 There are two principle types of EVA soling compounds used as shoe solings. The first is a crosslinked EVA usually microcellular in character, where the crosslinking is usually effected by peroxides. Such compounds can be bonded relatively easily by mechanically scouring the surface and then using a polychloroprene adhesive, or by wiping the mechanically prepared surface with an isocyanate primer prior to using a urethane adhesive. Alternatively it is possible to use a two-part urethane adhesive (a urethane adhesive to which an isocyanate has been added) on a mechanically prepared surface.

55 Good adhesion to thermoplastic EVA soling compounds is very much more difficult to achieve. We have found that a simple isocyanate treatment, a halogenating treatment, or a mixed isocyanate plus halogenation treatment is ineffective in promoting good adhesion. We have however unexpectedly found that good

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5	bonds to injection moulded thermoplastic EVA compounds can be obtained by treating the surface with a composition which can be used as a primer or directly as an adhesive.	solvent (when used) should be compatible with both primers and aromatic solvents can be used or e.g. chlorinated hydrocarbon solvents or solvent blends, e.g. of aromatic solvents and non-aromatic solvents of which a blend of three parts toluene to 1 part ethyl acetate is particularly suitable.	70
10	According to one form of the invention there is provided a method of shoe making in which an EVA-containing sole is injection moulded in situ onto a shoe upper, wherein the upper is treated with a composition comprising a mixture of a chlorinated polyolefin and a thermoplastic EVA, together with an adhesive if necessary. Preferably the mixture includes an organic polyisocyanate (as defined herein).	The vinyl acetate content of the EVA soling compound appears to influence the response to both methods of surface treatment and we consider that the vinyl acetate content should preferably be not less than 12 or more preferably 16% to ensure that these treatments are effective. The use of chlorinated rubber produces better response to low vinyl acetate copolymers than e.g. CP 343—1.	75
15	In particular, good bonds can be obtained by treating the upper surface with a solution of a mixture of a chlorinated polyolefin (such as that sold under the Eastman-Kodak product name CP 343—1 or chlorinated rubber as that sold by ICI under Trademark Allopren N20), and thermoplastic ethylene vinyl acetate copolymer (hereinafter called EVA copolymer) (such as that sold under the ICI product name EVA Resin 28—20) in xylene or other solvent followed by treatment of the surface with an organic polyisocyanate (such as 4—4' diphenylmethane diisocyanate e.g. as sold under the Trademark Caradate 30). By "poly" we mean two or more. The adhesion to such a prepared surface with a single or two-part urethane adhesive as used in the shoemaking industry (such as that sold under the trade name B.U. 8300) will be good. The concentration of chlorinated polyolefin and EVA copolymer in the solution can vary independently e.g. from 0.1% to 30% w/v, and the concentration of Caradate 30, for example in MEK, can vary e.g. from 1% to 30% w/v.	The mixed chlorinated polyolefin-EVA copolymerisocyanate primer, in particular, can be used to effect the bond between an upper material such as PVC, polyurethane or leather and an injection moulded-on EVA soling compound.	80
20	In order to simplify the bonding procedure we have found that it is possible and preferable to combine the two surface primers for use as a single primer. This mixed primer may comprise e.g. from 0.1% to 30% w/v of a chlorinated polyolefin plus e.g. from 0.1% to 30% of EVA copolymer plus e.g. from 0.1% to 30% w/v of the polyisocyanate dissolved in xylene or other aromatic solvent or solvent blend. Normally the total solids content of a primer solution will be from 5 to 10% w/v. After application of this primer a good bond is obtainable with a urethane adhesive. Normally it is not contemplated that the total of the three ingredients will exceed 30% w/v. However situations are possible where the primer will act similarly to an adhesive and in such cases the total content of the three ingredients may rise to 20% w/v or more.	The upper material may be coated with a urethane adhesive such as that sold under the Trademark B.U. 8300. This adhesive coated upper material is left for the adhesive to dry e.g. for 1 hour although longer drying periods can be used. The adhesive surface is then wiped with a xylene solution containing chlorinated polyolefin EVA copolymer and isocyanate. The treated adhesive surface is then left for at least 5 minutes before injection on the EVA soling compound. The concentration of chlorinated polyolefin and EVA copolymer in the xylene can vary independently e.g. from 0.1% to 30% w/v and the concentration of isocyanate can vary e.g. from 1% to 30% w/v.	85
25	In the Examples shown in Table 1, EVA compound UE 634 (Chemitrade Ltd) was injection moulded onto a full chrome upper leather (Steads Pearl Split), a PVC coated fabric (Blakes 47 thou patent PVC on S.D.I.), and a poromeric upper material (Porvair Limited) using the following procedure:	90	
30	Example 1. Leather — The surface to be treated was roughened with a wire brush and coated with urethane adhesive B.U. 8300 and left for 1 hour open time. A xylene solution containing 1.4% chlorinated polyolefin CP 343—1 plus 2.6% EVA Resin 28—20 plus 2.5% w/v Caradate 30 was applied to the adhesive surface. The treated leather was left for 5 minutes and 30 minutes respectively before injecting-on the UE 634 EVA soling compound.	95	
35	Example 2. P.V.C. — The surface was wiped with MEK and coated with urethane adhesive	100	
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B.U. 8300 and left for 1 hour open time. A xylene solution containing 1.4% w/v chlorinated polyolefin CP 343—1 plus 2.6% w/v EVA Resin 28—20 plus 2.5% w/v 4—4' diphenylmethane diisocyanate (Caradate 30) was applied and left for 5 minutes and 30 minutes respectively before injecting on the UE 634 EVA soling compound.

Example 3. — Porvair (Trade Mark) — The surface was roughened with a wire brush and coated with urethane adhesive B.U. 8300 and left for 1 hour open time. A xylene solution containing 1.4% w/v chlorinated polyolefin CP 343—1 plus 2.6% w/v EVA Resin 28—20 plus 2.5% w/v 4—4' diphenylmethane diisocyanate (Caradate 30) was applied and left for 5 minutes and 30 minutes respectively before injecting on the UE 634 EVA soling compound.

Example 4, 5 and 6. — Upper materials leather, PVC and Porvair were prepared as described in Examples 1, 2 and 3 respectively. The prepared surfaces were then each coated with a xylene solution containing 7% w/v chlorinated polyolefin CP 343—1 plus 13% w/v EVA Resin 28—20 plus 5% w/v 4—4' diphenylmethane diisocyanate (Caradate 30) and left for 1 hour open time before injecting on the UE 634 EVA soling compound.

TABLE I

ADHESIVE	TIME BETWEEN PRIMING AND MOULDING	Example 1 LEATHER UPPER		Example 2 PVC UPPER		Example 3 PORVAIR UPPER	
		LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE
B.U. 8300	No prime	0.8	10SSM 90ASM	0	100ASM	0.2	100ASM
	5 mins	6.2	55SM 95ASM	6.2	1.5SSM 40ASM 45AUP	5.0	100ASM
	30 mins	7.4	10SSM 90ASM	7.5	100ASM	5.9	100 ASM

Key:— ASM — failure of adhesion to soling material

SSM — surface soling material failure

AUP — failure of adhesion to upper plastic

TABLE 2

ADHESIVE	OPEN TIME OF ADHESIVE OF UPPER	Example 4 LEATHER UPPER			Example 5 PVC UPPER			Example 6 PORVAIR UPPER		
		LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE	
7% chlorinated polyolefin CP 343-1 plus 13% EVA, (I.C.I. 28-20) plus 5% Caradate 30	1 hour	3.4	20SM 80AUC SM tore	9.7	25SM 75AUP	5.9	100AUM UM tore			
	2 hours	8.4	80SM 20AUC SM tore	4.3	100 AUP	6.9	SSM 95AUM UM tore			

Key:- SM - soling material failure

AUC - adhesion to upper leather failure

AUP - adhesion to upper material failure

AUM - adhesion to upper material failure

SM tore - soling material failure tore

UM tore - upper material tore

WHAT WE CLAIM IS:—

1. A method of shoe making in which an EVA-containing sole is injection moulded in situ onto a shoe upper, wherein the upper is treated with a composition comprising a mixture of a chlorinated polyolefin and a thermoplastic EVA, together with an adhesive if necessary.

5 2. A method as claimed in claim 1 wherein the mixture includes an organic polyisocyanate (as defined herein).

10 3. A method as claimed in claim 1 or claim 2 wherein the composition is in the form of a solution of the said mixture in a solvent and is applied as a primer, wherein the total solids content of the solution does not exceed 30% w/v.

15 4. A method as claimed in claim 3 wherein the solution has a total solids content of 5% to 10% w/v.

20 5. A method as claimed in claim 2 wherein the composition is in the form of a solution of the said mixture in a solvent, and is applied as an adhesive, wherein the total solids content of the solution is 20% w/v or more.

25 6. A method as claimed in any of claims 3, 4 or 5 wherein the solvent used in the solution comprises xylene or a blend of an aromatic solvent with a non-aromatic solvent.

30 7. A method as claimed in any preceding claim wherein the chlorinated polyolefin is chlorinated natural rubber.

35 8. A method as claimed in any preceding claim substantially as described herein with reference to any one of the Examples.

9. A shoe prepared by a method as claimed in any preceding claim.

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